Supporting Information For

D-glucosamine—a novel and natural ligand for the \( N \)-arylation of imidazoles with aryl and heteroaryl bromides catalyzed by CuI

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**General Consideration.** All reactions were carried out in Schlenk tube, and run under an atmosphere of N\(_2\). All the copper sources, ligands and bases were commercially available. All products were confirmed by \(^1\)H NMR, \(^{13}\)C NMR. Unknown compound was additionally confirmed by Elemental analysis.

**Typical Procedure**

A Schlenk tube equipped with a Teflon valve was charged with a magnetic stir bar, Cs\(_2\)CO\(_3\) (684mg, 2.1mmol), CuI (0.38mg, 0.20mmol, 20mol%), and D-glucosamine hydrochloride (83mg, 0.40mmol, 40mol%). The tube was evacuated and backfilled with N\(_2\) (this procedure was repeated three times). Under a counter flow of N\(_2\), DMSO (0.5mL) was added by syringe at room temperature and pre-stirred for 0.5 h. Then a solution of bromobenzene (188mg, 1.2mmol), imidazole (68mg, 1.0mmol) in DMSO (0.5mL) was added via syringe under a counter flow of N\(_2\). The tube was sealed and the mixture was allowed to stir for 24 h at 110°C temperature. H\(_2\)O (5mL) was added to the reaction mixture after the completion of the reaction. Then it was extracted with (20mL×3) ethyl acetate and the combined organic layer was dried by Na\(_2\)SO\(_4\), concentrated by vacuum. The residue was purified by column chromatography on silica gel using hexane/ethyl acetate (1:3) as eluent to give an oil of 1-phenylimidazole (121mg, 84%), **3a**: 1-(phenyl)-1H-imidazole\(^1\)

\(^1\)H NMR (400MHz, CDCl\(_3\)/TMS): \(\delta\) 7.86 (s, 1H), 7.50-7.21 (m, 7H), \(^{13}\)C NMR (100MHz, CDCl\(_3\)/TMS): \(\delta\) 137.2, 135.5, 130.3, 129.8, 127.4, 121.4, 118.2.

**3b**: 1-(4-methylphenyl)-1H-imidazole\(^1\)

m.p.: 45–46°C, \(^1\)H NMR (400MHz, CDCl\(_3\)/TMS): \(\delta\) 7.80 (s, 1H), 7.26-7.18 (m, 6H), 2.39 (s, 3H) \(^{13}\)C NMR (100MHz, CDCl\(_3\)/TMS): 137.4, 135.6, 134.9, 130.3, 130.2, 121.3, 118.3, 20.9.

**3c**: 1-(2-methylphenyl)-1H-imidazole\(^1\)

\(^1\)H NMR (400MHz, CDCl\(_3\)/TMS): \(\delta\) 7.58 (s, 1H), 7.35-7.32 (m, 2H), 7.30-7.27 (m, 1H), 7.22-7.20 (m, 2H), 7.05 (s, 1H), 2.18 (s, 3H) \(^{13}\)C NMR (100MHz, CDCl\(_3\)/TMS): 137.3, 136.5, 133.7, 131.1, 129.2, 128.6, 126.7, 126.4, 120.3, 17.4.

**3d**: 1-(4-methoxyphenyl)-1H-imidazole\(^1\)

\(^1\)H NMR (400MHz, CDCl\(_3\)/TMS): \(\delta\) 7.74 (s, 1H), 7.30-7.27 (m, 2H), 7.19-7.17 (m,
2H), 6.98-6.96 (m, 2H), 3.83 (s, 3H), $^{13}$C NMR (100MHz, CDCl$_3$/TMS): δ 158.8, 135.7, 130.6, 129.9, 123.0, 118.6, 114.8, 55.4.

3e: 1-(3, 4-dimethoxyphenyl)-1H-imidazole

$^1$H NMR (400MHz, CDCl$_3$/TMS): δ 7.77 (s, 1H), 7.22 (s, 1H), 7.19 (s, 1H), 6.93-6.88 (m, 3H), 3.92 (s, 6H), $^{13}$C NMR (100MHz, CDCl$_3$/TMS): δ 149.7, 148.6, 135.9, 130.9, 130.0, 118.8, 114.1, 111.6, 106.2, 56.2, 56.1.

3f: 1-(4-fluorophenyl)-1H-imidazole

$^1$H NMR (400MHz, CDCl$_3$/TMS): δ 7.78 (s, 1H), 7.37-7.33 (m, 2H), 7.21-7.14 (m, 4H), $^{13}$C NMR (100MHz, CDCl$_3$/TMS): δ 162.8, 160.3, 134.7 (J=194.4Hz), 130.3, 123.4 (J=8.2Hz), 118.5, 116.6 (J=22.7Hz).

3g: 1-(4-trifluoromethylphenyl)-1H-imidazole

m.p.: 69-70°C, $^1$H NMR (400MHz, CDCl$_3$/TMS): δ 7.93 (s, 1H), 7.76 (d, J=8.0Hz, 2H), 7.53 (d, J=8.0Hz, 2H), 7.34 (s, 1H), 7.27 (s, 1H), $^{13}$C NMR (100MHz, CDCl$_3$/TMS): δ 139.9, 135.4, 131.1, 129.5 (J=29.6, 62.5Hz), 127.2, 123.6 (J=272.1, 549.0Hz), 121.2, 117.8.

3h: 1-(3, 5-bis(trifluoromethyl)phenyl)-1H-imidazole

m.p.: 93-95°C, $^1$H NMR (400MHz, CDCl$_3$/TMS): δ 7.93 (s, 1H), 7.87 (s, 1H), 7.83 (s, 2H), 7.34 (s, 1H), 7.27 (s, 1H), $^{13}$C NMR (100MHz, CDCl$_3$/TMS): δ 138.4, 135.3, 133.6 (J=33.7, 68.6Hz), 131.6, 122.4 (J=271.7, 543.1Hz), 121.2, 120.9, 117.8. Anal. Calc. for C$_{11}$H$_6$F$_6$N$_2$: C, 47.16; H, 2.16; N, 10.00. Found: C, 47.30; H, 2.09; N, 9.82%.

3i: 1-(1-naphthalenyl)-1H-imidazole

m.p.: 61-63°C, $^1$H NMR (400MHz, CDCl$_3$/TMS): δ 7.93 (d, J=8.0Hz, 2H), 7.75(s, 1H), 7.60-7.41 (m, 5H), 7.29 (s, 1H), 7.23 (s, 1H), $^{13}$C NMR (100MHz, CDCl$_3$/TMS): δ 138.3, 134.1, 133.9, 129.4, 129.4, 129.2, 128.2, 127.5, 126.9, 125.1, 123.54, 122.2, 121.6.

3j: 1-(2-naphthalenyl)-1H-imidazole

m.p.: 122-123°C, $^1$H NMR (400MHz, CDCl$_3$/TMS): δ 7.97-7.81 (m, 5H), 7.59-7.51 (m, 3H), 7.40 (s, 1H), 7.26 (s, 1H), $^{13}$C NMR (100MHz, CDCl$_3$/TMS): δ 135.8, 134.7, 133.5, 132.1, 130.5, 130.0, 127.8, 127.8, 127.3, 126.5, 120.2, 119.0, 118.4.
3k: 1-(4-acetamidophenyl)-1H-imidazole
m.p.: 164-166˚C, $^1$H NMR (400MHz, CDCl$_3$/TMS): δ 10.08 (s, 1H), 8.16 (s, 1H), 7.70 (d, $J$ = 8.8Hz, 2H), 7.66 (s, 1H), 7.55 (d, $J$ = 9.2Hz, 2H), 7.08 (s, 1H), $^{13}$C NMR (100MHz, DMSO/TMS): δ 168.9, 138.8, 135.8, 132.5, 130.2, 121.3, 120.3, 118.3, 24.2. Anal. Calc. for C$_{11}$H$_{11}$N$_3$O: C, 65.66; H, 5.51; N, 20.88. Found: C, 65.78; H, 5.55; N, 20.68%.

3l: 1-(2-trifluoroacetamido-5-methylphenyl)-1H-imidazole
m.p.: 178-180˚C, $^1$H NMR (400MHz, CDCl$_3$/TMS): δ 11.06 (s, 1H), 7.77 (s, 1H), 7.42-7.28 (m, 4H), 7.06 (s, 1H), 2.38 (s, 3H), $^{13}$C NMR (100MHz, DMSO/TMS): 156.0 ($J$=36.6, 73.0Hz), 139.5, 133.8, 129.7, 129.3, 129.0, 127.3, 126.6, 120.3, 116.2 ($J$=287.0, 573.9Hz), 20.8. Anal. Calc. for C$_{12}$H$_{10}$F$_3$N$_3$O: C, 53.54; H, 3.74; N, 15.61. Found: C, 53.48; H, 3.90; N, 15.49%.

3m: 1-(pyridine-2-yl)-1H-imidazole
$^1$H NMR (400MHz, CDCl$_3$/TMS): δ 8.46 (s, 1H), 8.35 (s, 1H), 7.82-7.77 (m, 1H), 7.64-7.63 (t, 1H), 7.36-7.33 (m, 1H), 7.24-7.19 (m, 2H). $^{13}$C NMR (100MHz, CDCl$_3$/TMS): δ 149.1, 138.9, 134.9, 130.5, 121.9, 116.0, 112.2.

3n: 1-(pyridine-3-yl)-1H-imidazole
$^1$H NMR (400MHz, CDCl$_3$/TMS): δ 8.71 (d, 1H), 8.60-8.58 (m, 1H), 7.84 (s, 1H), 7.42-7.39 (m, 1H), 7.27-7.25 (m, 1H), 7.21 (s, 1H), $^{13}$C NMR (100MHz, CDCl$_3$/TMS): 148.7, 142.8, 135.5, 133.8, 131.1, 128.8, 124.2, 118.0.

3o: 1-(thien-2-yl)-1H-imidazole
$^1$H NMR (400MHz, CDCl$_3$/TMS): δ 7.81 (s, 1H), 7.43 (dd, 1H), 7.24-7.17 (m, 4H), $^{13}$C NMR (100MHz, CDCl$_3$/TMS): δ 136.2, 135.7, 129.9, 127.1, 121.3, 118.4, 113.1.

3p: 1-(thien-3-yl)-1H-imidazole
m.p.: 81-83˚C, $^1$H NMR (400MHz, CDCl$_3$/TMS): δ 7.79 (s, 1H), 7.41 (dd, 1H), 7.21-7.14 (m, 4H), $^{13}$C NMR (100MHz, CDCl$_3$/TMS): 136.2, 135.8, 129.9, 127.1, 121.4, 118.5, 113.2.

3q: 1-(6-methoxy-pyridine-3-yl)-1H-imidazole
m.p.: 186-188˚C, $^1$H NMR (400MHz, CDCl$_3$/TMS): δ 8.24 (t, 1H), 7.75 (s, 1H), 7.61-7.58 (t, 1H), 7.22-7.18 (t, 2H), 6.87-6.85 (dd, 1H), 3.98 (s, 3H), $^{13}$C NMR
(100MHz, CDCl₃/TMS): 163.3, 140.3, 136.0, 133.1, 130.5, 128.3, 118.8, 111.7, 53.9.

3r: 2-(1H-imidazol-1-yl)-pyrimidine¹
m.p.: 122-123°C, ¹H NMR (400MHz, CDCl₃/TMS): δ 8.68-8.67 (d, 2H), 8.60 (s, 1H), 7.87 (t, 1H), 7.19-7.15 (m, 2H), ¹³C NMR (100MHz, CDCl₃/TMS): δ 158.7, 154.7, 136.1, 130.6, 118.8, 116.5.

3s: 1-phenyl-1H-benzimidazole²
m.p.: 96-98°C, ¹H NMR (400MHz, CDCl₃/TMS): δ 8.11 (s, 1H), 7.90-7.88 (m, 1H), 7.58-7.43 (m, 6H), 7.36-7.30 (m, 2H), ¹³C NMR (100MHz, CDCl₃/TMS): δ 143.9, 142.3, 136.2, 133.6, 129.9, 127.9, 123.9, 123.6, 122.7, 120.5, 110.3.
